FORM PTO-1390 (Modified) (REV 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: FA-1058

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): 10/069036

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/07994	16 AUGUST 2000 (16.08.00)	17 AUGUST 1999 (17.08.99)

TITLE OF INVENTION

CLEANING AGENT AND METHOD FOR CLEANING ULTRAFILTRATION MEMEBRANES IN ELECTROPHORETIC DIP COATING INSTALLATIONS

APPLICANT(S) FOR DO/EO/US

LEHMANN, Horst et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☑ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☑ This is an express request to being national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b)) and PCT Articles 22 and 39(1).
4. ☑ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☑ A copy of the International Application was filed (35 U.S.C. 371 (c) (2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau.
   b. ☐ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☑ A translation of the International Application into English (35 U.S.C. 371 (c) (2)).
7. ☑ A copy of the International Search Report (PCT/ISA/210).
8. ☑ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c) (3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
10. ☑ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☑ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included :

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☑ A FIRST preliminary amendment.
    A SECOND or SUBSEQUENT preliminary amendment.
16. ☐ A substitute specification.
17. ☑ A change of power of attorney and/or address letter.
18. ☑ Certificate of Mailing by Express Mail.
19. ☐ Other items or information:

17. General Power of Attorney
18. Express Mailing Label No.: EJ376013594US

APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/069036	PCT/EP00/07994	FA-1058

20. The following fees are submitted

CALCULATIONS PTO USE ONLY

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) – (5)) :

☑ Search Report has been prepared by the EPO or JPO	$890.00	
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482)	$710.00	
☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	$740.00	
☐ Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	$1,040.00	
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) And all claims satisfied provisions of PCT Article 33(2)-(4)	$ 100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT	=	**$890.00**
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).		**$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims	19 - 20 =	0	x $18.00	**$0.00**
Independent Claims	1 - 3 =	0	x $84.00	**$0.00**
Multiple Dependent Claims **(check if applicable)**			☐	**$0.00**

TOTAL OF ABOVE CALCULATIONS	=	**$0.00**
Reduction of ½ for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable).** ☐		**$0.00**
SUBTOTAL	=	**$0.00**
Processing Fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).		**$0.00**
TOTAL NATIONAL FEE	=	**$890.00**
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐		**$0.00**
TOTAL FEES ENCLOSED	=	**$890.00**
	Amount to be : refunded	$
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☐ A check in the amount of _____ to cover the above fees enclosed.

☑ Please charge my Deposit Account No. **04-1928** in the amount of **$890.00** to cover the above fees.

☑ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **04-1928** a duplicate copy of this sheet is enclosed.

NOTE : Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (CFR 1.37(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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36,087
REGISTRATION NUMBER

02-15-02
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Horst Lehmann et al.

Art Unit: UNKNOWN

Serial No.: UNKNOWN

Examiner: UNKNOWN

Filed: Concurrently Herewith

Atty. Docket: FA1058

For: CLEANING AGENT AND METHOD FOR CLEANING ULTRAFILTRATION MEMBRANES IN ELECTROPHORETIC DIP COATING INSTALLATIONS

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

It is respectfully requested that the Examiner enter these amendments prior to examination of the above-identified application on its merits. Please amend the application as follows:

IN THE SPECIFICATION:

Please insert the following subtitles:

Page 1, line 6, **Background of the Invention**

Page 3, line 5, **Summary of the Invention**

Page 3, line 13, **Detailed Description of the Invention**

Page 10, line 25, **Examples**

IN THE CLAIMS:

Please cancel claims 1-11 without prejudice to the Applicants.

Please add new claims 12-30 as follows:

Claim 12. An aqueous cleaning agent for ultrafiltration membranes in ultrafiltration units of electro-dipcoating plants comprising an electro-dipcoating lacquer binder, wherein the electro-dipcoating lacquer

binder is overneutralized with a neutralizing agent corresponding to a degree of neutralization of the binder of at least 100 to 1000%.

Claim 13. The aqueous cleaning agent according to claim 12, further comprising up to10 wt.% of an organic solvent.

Claim 14. The aqueous cleaning agent according to claim 13, wherein the organic solvent is a water-soluble solvent.

Claim 15. The aqueous cleaning agent according to claim 12, wherein the aqueous cleaning agent contains the electro-dipcoating lacquer binder in an amount ranging from 5 to 35 wt.%.

Claim 16. The aqueous cleaning agent according to claim 12, wherein the electro-dipcoating lacquer binder is selected from the group consisting of an anodic dipcoating lacquer binder and a cathodic electro-dipcoating binder.

Claim 17. The aqueous cleaning agent according to claim 16, wherein the anodic dipcoating lacquer binder is selected from the group consisting of anodic dipcoating lacquer binders containing anionic-groups and anodic dipcoating lacquer binders containing groups that have been converted into anionic-groups, wherein the resin has an acid number ranging from 35 to 300 mg KOH/g.

Claim 18. The aqueous cleaning agent according to claim 17, wherein the anodic dipcoating lacquer binder is selected from the group consisting of polyesters, epoxy resin esters, (meth)acrylic copolymer resins, maleate oils and polybutadiene oils.

Claim 19. The aqueous cleaning agent according to claim 17, wherein the anodic dipcoating lacquer binder is self-crosslinking.

Claim 20. The aqueous cleaning agent according to claim 17, wherein the anodic dipcoating lacquer is the binder and a cross-linking agent.

Claim 21. The aqueous cleaning agent according to claim 16, wherein the cathodic dipcoating lacquer binder is selected from the group consisting of cathodic dipcoating lacquer binders containing cationic-groups and basic groups that have been converted into cationic-groups, wherein the resin has an amine number ranging from 20 to 250 mg KOH/g.

Claim 22. The aqueous cleaning agent according to claim 21, wherein the cathodic dipcoating lacquer binder is selected from the group consisting of amino(meth)acrylic resins, aminopolyurethane resins, polybutadiene resins containing amino groups, aminoepoxy resins and epoxy resin-carbon dioxide-amine reaction products.

Claim 23. The aqueous cleaning agent according to claim 21 wherein the cathodic dipcoating lacquer binder is self-crosslinking.

Claim 24. The aqueous cleaning agent according to claim 21, wherein the cathodic dipcoating lacquer is the binder and a crosslinking agent.

Claim 25. The aqueous cleaning agent according to claim 12, wherein the electro-dipcoating lacquer binder is an anodically depositable binder and the neutralizing agent is a base.

Claim 26. The aqueous cleaning agent according to claim 25, wherein the neutralizing agent is selected from the group consisting of amine and amino alcohols.

Claim 27. The aqueous cleaning agent according to claim 12, wherein the electro-dipcoating lacquer binder is a cathodically depositable binder and the neutralizing agent is an acid.

Claim 28. The aqueous cleaning agent according to claim 27, wherein the neutralizing agent is selected from the group consisting of organic monocarboxylic acids and sulfonic acids.

Claim 29. A process for cleaning electro-dipcoating ultrafiltration membranes comprising the step of circulating the aqueous cleaning agent of claim 12 through an ultrafiltration module of an electro-dipcoating lacquer ultrafiltration unit operated on an industrial scale at a throughput ranging from 2 to 20 m^3 per hour.

Claim 30. The process according to claim 29, further comprising adding the aqueous cleaning agent to an electro-dipcoating bath subsequent to cleaning, wherein the electro-dipcoating bath comprises the same components as the cleaning agent.

REMARKS

Appropriate subtitles have been inserted into the specification. Claims 1-11 have been cancelled. Claims 12-30 are submitted herewith in a format acceptable to the United States Patent and Trademark Office. If the Examiner has questions regarding the application or the contents of this Preliminary Amendment, the Examiner is invited to contact the undersigned at the number provided.

Respectfully submitted,

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Date: February 13, 2002

Cleaning agent and process for cleaning ultrafiltration membranes in electro-dipcoating plants

The invention relates to cleaning agents for ultrafiltration membranes in ultrafiltration units of electro-dipcoating plants. The invention relates also to a process for cleaning ultrafiltration membranes using the cleaning agents.

Electro-dipcoating (EDC) is widely used in industrial lacquering both as anodic dipcoating (ADC) and, especially, as cathodic dipcoating (CDC). In particular, it is used, for example, as CDC in the automotive industry for applying the anticorrosive primer coating layer to motor vehicle bodies. The EDC baths are coupled with an ultrafiltration unit having one or more ultrafiltration modules, in which unit the electro-dipcoating lacquer (EDL) is subjected to membrane pressure filtration at, for example, from 1 to 5 bar (initial pressure at the ultrafiltration module). During the ultrafiltration, the EDC coating composition is separated at a semi-permeable membrane into a concentrate, which is fed back into the EDC bath, and an EDL ultrafiltrate (permeate). The EDL ultrafiltrate has only a low solids content of, for example, from greater than 0 to less than 0.5 wt.%. It consists mainly of water, and it contains to a subordinate degree constituents of the electro-dipcoating lacquer that pass through the membrane, such as neutralising agents, dissolved salts, organic solvents and low molecular weight binder constituents. The EDL ultrafiltration has two functions. On the one hand, the EDL ultrafiltrate that is obtained is used to rinse non-adhering EDC lacquer from the EDL-coated substrates after they emerge from the EDL coating bath. After rinsing, the EDL-coated substrates are conveyed to the stoving furnace of the EDC plant. The EDL rinsed off with the EDL ultrafiltrate is fed back to the EDC bath again. The second function of the EDL ultrafiltration is that of keeping the composition of the EDC bath constant within a certain tolerance, which is achieved by the discarding of a portion of the EDL ultrafiltrate that is not used as rinsing agent. In that manner, it is possible to

prevent disruptive constituents that pass through the membrane from building up in the EDC bath.

The separating membranes within the ultrafiltration modules of EDL ultrafiltration units require cleaning at intervals and, generally, also conditioning (impregnation) before being used for their intended purpose. US-A 4 136 025, for example, describes a process for cleaning membranes within CDL ultrafiltration units using an aqueous solution of an acid containing a water-soluble organic solvent. The example mentioned in US-A 4 136 025 gives the following as the composition of the aqueous cleaner solution:

7.5 wt.% butyl glycol,
5.7 wt.% 88 % aqueous lactic acid, and
86.8 wt.% deionised water.

The cleaning action of such cleaning agents of the prior art consisting essentially of neutralising agent, water and organic solvent is in need of improvement. For example, it has been found that, following membrane cleaning using cleaning agents having such a composition, the performance of the EDL ultrafiltration units declines ever more rapidly from cleaning interval to cleaning interval in the sense of an exponential function, that is to say the cleaning intervals become shorter from one cleaning operation to the next until cleaning is no longer worthwhile and the membrane or the ultrafiltration modules containing the membrane have to be replaced. In addition, the performance of the EDL ultrafiltration units becomes poorer and poorer from cleaning interval to cleaning interval as compared with the performance following each preceding cleaning operation. Such disadvantages of the use of cleaning agents of the prior art are particularly pronounced in connection with the cleaning of modern EDL ultrafiltration modules of compact construction.

The object of the invention is to provide cleaning agents that are more effective as compared with the prior art, and processes for cleaning EDL ultrafiltration membranes.

The object can be achieved if aqueous cleaning agents containing EDL binders overneutralised with neutralising agent are used for the cleaning of EDL ultrafiltration membranes, for example ultrafiltration membranes contained in EDL ultrafiltration modules of EDL ultrafiltration units.

The invention provides aqueous cleaning agents that can be used for the cleaning of EDL ultrafiltration membranes and that contain EDL binders overneutralised with neutralising agent. The aqueous cleaning agents may be either aqueous cleaning agents that can be used for the cleaning of ADL ultrafiltration membranes, which agents contain ADL binders overneutralised with base, or they are aqueous cleaning agents that can be used for the cleaning of CDL ultrafiltration membranes and that contain CDL binders overneutralised with acid.

It is fundamental to the invention that the cleaning agents according to the invention contain, in addition to water, EDL binders, for example corresponding to a solids content of from 5 to 35 wt.%. The content of EDL binders in the cleaning agents according to the invention is preferably from 10 to 30 wt.%, particularly preferably from 15 to 28 wt.%.

The ADL binders contained in the cleaning agents according to the invention for the cleaning of ADL ultrafiltration membranes are conventional ADL binders carrying anionic groups or groups that can be converted into anionic groups, for example COOH, SO_3H and/or PO_3H_2 groups. COOH groups are preferred. The acid numbers of such resins are, for example, from 35 to 300 mg KOH/g. The weight-average molar mass (Mw) of the resins is preferably from 300 to 10,000. Examples of ADL binders are polyesters, epoxy resin esters, (meth)acrylic copolymer resins, maleate oils or polybutadiene oils. The ADL binders can be self-crosslinking or can be used in admixture with known crosslinking agents. Examples of such crosslinking agents are aminoplastic resins, for example based on triazine, crosslinking agents containing transesterifiable groups, or blocked polyisocyanates.

The CDL binders contained in the cleaning agents according to the invention for the cleaning of CDL ultrafiltration membranes are conventional CDL binders containing cationic groups or basic groups that can be converted into cationic groups, for example amino, ammonium, e.g. quaternary ammonium, phosphonium and/or sulfonium groups. Preference is given to CDL binders having basic groups, particularly preferably having nitrogen-containing basic groups, such as amino groups. Such basic resins are, for example, resins containing primary, secondary and/or tertiary amino groups. Some or all of the tertiary amino groups may be present in quaternised form. The amine numbers of such resins are, for example, from 20 to 250 mg KOH/g. The weight-average molar mass (Mw) of the resins is preferably from 300 to 10,000. Examples of CDL binders are amino(meth)acrylate resins, aminopolyurethane resins, polybutadiene resins containing amino groups, aminoepoxy resins, and also epoxy resin-carbon dioxide-amine reaction products. The CDL binders can be self-crosslinking or can be used in admixture with known crosslinking agents. Examples of such crosslinking agents are aminoplastic resins, crosslinking agents having terminal double bonds, polyepoxy compounds, crosslinking agents having cyclic carbonate groups, crosslinking agents containing transesterifiable and/or transamidatable groups, and, especially, blocked polyisocyanates.

In connection with the cleaning agents according to the invention, the term "EDL binders" means EDL binders as such or EDL binders plus crosslinking agents for the EDL binders. The cleaning agents according to the invention can, therefore, contain EDL binders, for example self-crosslinking EDL binders, or EDL binders and crosslinking agents.

It is preferred for the cleaning agents according to the invention to contain the same EDL binders and, optionally, crosslinking agents as the EDL baths whose ultrafiltration systems are cleaned using the cleaning agents according to the invention.

In addition to water and EDL binders, the aqueous cleaning agents according to the invention contain neutralising agents corresponding to an overneutralisation of the EDL binders, for example corresponding to a degree of neutralisation of the EDL binders of

from more than 100 to 1000 %. Preferred examples of bases used as neutralising agents for ADL binders are bases conventionally employed in ADL's, such as amines or amino alcohols. Preferred examples of acids used as neutralising agents for CDL binders are acids conventionally employed in CDL's, such as organic monocarboxylic acids, such as, for example, lactic acid, formic acid, acetic acid, or sulfonic acids, such as, for example, amidosulfonic acid, N-alkylamidosulfonic acid, methanesulfonic acid. It is preferred for the cleaning agents according to the invention to contain the same neutralising agents as the EDL baths whose ultrafiltration systems are cleaned using the cleaning agents according to the invention.

The aqueous cleaning agents according to the invention can contain organic solvents, for example preferably in an order of magnitude as in the EDL bath, for example of up to 10 wt.%, preferably from 0 to 5 wt.%. Particularly preferably, they contain from 0 to less than 1 wt.% organic solvents. Examples of organic solvents are especially water-soluble organic solvents, such as glycol ethers, for example butyl glycol, ethoxypropanol; alcohols, such as isopropanol, isobutanol, n-butanol. If the cleaning agents according to the invention contain organic solvents, it is preferred for them to contain the same solvents as the EDL baths whose ultrafiltration systems are cleaned using the cleaning agents according to the invention.

The cleaning agents according to the invention can be prepared by mixing together, in the desired relative proportions, EDL binders and, optionally, crosslinking agents, neutralising agents and water as well as, optionally, organic solvents. Instead of water, it is also possible to use EDL ultrafiltrate. For example, the cleaning agents according to the invention can be prepared by mixing together, in the appropriate relative proportions, an aqueous EDL dispersion containing underneutralised or completely neutralised EDL binders and, optionally, crosslinking agents, and neutralising agents in an amount sufficient to overneutralise the EDL binders, water (or EDL ultrafiltrate) and, optionally, organic solvents.

EDL dispersions are aqueous dispersions of EDL binders and, optionally, crosslinking agents for the EDL binders. The EDL binders are present in the EDL dispersions in a

form neutralised with neutralising agent. They may be underneutralised or completely neutralised. Complete neutralisation is here not to be confused with 100 % neutralisation, but is always less than 100 %. Complete neutralisation is present when the afore-described amount of neutralising agent has been used for neutralising the EDL binders, and corresponds, in the case of both ADL binders and CDL binders, to degrees of neutralisation of, for example, from 40 % to, for example, not more than 60 %, based on the EDL binder as such. When complete neutralisation is exceeded, the term overneutralisation is used. EDL dispersions have solids contents of, for example, from 30 to 45 wt.% and a content of organic solvents of preferably less than 5 wt.%, based on the dispersion solids.

EDL dispersions can be prepared by synthesising EDL binders in the presence or absence of organic solvents and converting the resulting binders into an aqueous dispersion by dilution with water of the EDL binders previously neutralised with neutralising agent. The EDL binder(s) may be present in admixture with one or more suitable crosslinking agents and can be converted into the aqueous dispersion together therewith. Organic solvent, where present, can be removed to the desired content before or after the conversion into the aqueous dispersion, for example by distillation *in vacuo*. It is possible to avoid the subsequent removal of solvents if, for example, the EDL binders optionally present in admixture with crosslinking agents are neutralised with neutralising agent in the low-solvent or solvent-free state, for example in the form of a solvent-free melt at temperatures of, for example, up to 140°C, and are then converted into the EDL dispersion with water. It is likewise possible, for example, to avoid the removal of organic solvents if the EDL binders are used initially in the form of a solution in a radically polymerisable, olefinically unsaturated monomer, or the binder synthesis is carried out in a radically polymerisable monomer (e.g. styrene) as solvent, conversion into an aqueous dispersion is then carried out by neutralisation with neutralising agent and dilution with water, and the radically polymerisable monomer is subsequently removed by polymerisation.

The cleaning agents according to the invention can be used for cleaning EDL ultrafiltration membranes. Accordingly, the invention relates also to a process for

cleaning EDL ultrafiltration membranes using the cleaning agents according to the invention.

The process according to the invention is suitable for the cleaning of membranes in EDL ultrafiltration systems, irrespective of the type of ultrafiltration module in question. Examples of different types of EDL ultrafiltration modules are plate-type ultrafiltration modules, tubular ultrafiltration modules, tube-bundle ultrafiltration modules, as well as spiral wound ultrafiltration modules, which are particularly compact in construction.

The process according to the invention is not subject to any limitations as regards the nature of the ultrafiltration membranes, for example as regards the membrane material and the pore size, but is suitable for cleaning all ultrafiltration membranes conventionally used in EDL ultrafiltration units. Examples of membrane materials are polysulfones, polyether sulfones, polyvinylidene fluoride, polyacrylonitrile; the pore widths of the ultrafiltration membranes to be cleaned by the process according to the invention are, for example, from 5 to 100 nm.

The cleaning process according to the invention is not subject to any limitations regarding the composition of the EDL baths ultrafiltered by the EDL ultrafiltration membranes that are to be cleaned.

The cleaning of EDL ultrafiltration membranes is generally carried out whenever the ultrafiltration performance, which is expressed as the flux rate (volume of ultrafiltrate per unit time), declines markedly and falls below a defined limiting value or a defined fraction of the initial performance.

For the purposes of cleaning, the EDL ultrafiltration operation is interrupted, either with the EDL coating process being maintained or with the EDL coating process being interrupted. It is possible to maintain the EDL coating process, for example, when the EDL ultrafiltration unit has a plurality of ultrafiltration modules and only one ultrafiltration module or some of the ultrafiltration modules are cleaned by the process

according to the invention, while the remaining ultrafiltration modules continue to operate in the intended manner.

If all the ultrafiltration modules are cleaned simultaneously by the process according to the invention, the EDL coating process can optionally be interrupted, for example if an inadequate supply of EDL ultrafiltrate is available for bridging the duration of the cleaning operation. For cleaning, EDL bath material present in the EDL ultrafiltration unit is rinsed out with water or EDL ultrafiltrate and fed back to the EDL bath. The cleaning agent according to the invention is then circulated through the EDL ultrafiltration unit.

The throughput of cleaning agent according to the invention is high; for example, the throughput of cleaning agent according to the invention circulated through an ultrafiltration module that is to be cleaned of an EDL ultrafiltration unit operated on an industrial scale may be from 2 to 20 m^3 per hour. Rinsing with the cleaning agent according to the invention is carried out, for example, in the same pressure range (initial pressure at the EDL ultrafiltration module in question) as the ultrafiltration of the EDL bath material, preferably in the range from more than 1 to 2 bar. In general, the cleaning agent according to the invention is itself separated into a concentrate and an ultrafiltrate, it being preferred for the two components to be added again to the circulating cleaning agent.

The cleaning agents according to the invention can be used for the cleaning of EDL ultrafiltration membranes either immediately after their preparation, by mixing of their constituents, or after a maturing time of, for example, up to 12 hours has first been allowed to elapse. The cleaning agent according to the invention can be used for the cleaning of the EDL ultrafiltration membranes at a temperature of, for example, from 20 to 60°C, preferably from 40 to 55°C. The duration of the cleaning operation is, for example, from 5 to 24 hours. The cleaning parameters of cleaning agent throughput, pressure, temperature and duration can be worked out or optimised in each individual case by the person skilled in the art by means of simple tests.

When the cleaning operation is complete, the cleaning agent can be discarded or, if its cleaning action is still adequate, can be stored for further use in subsequent cleaning cycles.

In a preferred embodiment, the process according to the invention is carried out using an aqueous cleaning agent that contains the same EDL binder(s) and, optionally, crosslinking agent(s) as well as the same neutralising agent and, if the aqueous cleaning agent contains organic solvents, the same organic solvents as the EDL baths whose ultrafiltration systems are cleaned using the cleaning agent according to the invention. The cleaning agent then does not have to be discarded once the cleaning operation is complete, but can be added to the EDL bath in question, which contains the same binders and, optionally, crosslinking agents, the same neutralising agents and – where present – the same organic solvents. Such a procedure is particularly preferred because it does not give rise to any problems with regard to the disposal of the aqueous cleaning agents after they have been used according to the invention.

The addition of the used aqueous cleaning agent to the EDL bath causes the neutralising agent content to rise above the afore-mentioned complete neutralisation of the EDL binders, since the cleaning agent introduces overneutralised EDL binder into the EDL bath. In practice, however, that is usually of no or little significance. This becomes evident when the dimensions of industrial EDL coating plants are visualised. For example, EDL ultrafiltration systems are cleaned by the circulation of from 50 to 3000 litres of the aqueous cleaning agent according to the invention. When the cleaning operation is complete, that amount of used aqueous cleaning agent is added to the EDL bath having a volume of, for example, from 30 to 500 m^3, so that the increase in the neutralising agent content in the EDL bath is, ultimately, minimal. In the case of smaller baths, the amounts are correspondingly lower. If the increase in the neutralising agent content in the EDL bath cannot or is not to be tolerated, it is possible for the excess amount of neutralising agent in the EDL bath to be compensated for in the course of the solids compensation of the EDL bath that is necessary at regular intervals. During the EDL coating process, solids are discharged from the EDL bath as a result of the deposition of ED lacquer on the substrate. EDL baths therefore require regular

solids compensation, which can be effected, for example, by the addition of corresponding amounts of aqueous EDL dispersion and pigment paste to the EDL bath depleted of solids. The EDL dispersion can be completely neutralised, or it is underneutralised and the amount of neutralising agent required for complete neutralisation is added separately. The afore-mentioned compensation of the excess neutralising agent in the EDL bath can, therefore, be carried out by using, in the solids compensation of the EDL bath, an appropriate amount of underneutralised EDL dispersion and/or a correspondingly smaller amount of neutralising agent in the case of the separate addition of neutralising agent.

The cleaning agents according to the invention and the cleaning process according to the invention permit effective cleaning of EDL ultrafiltration membranes. The cleaning intervals are long and the performance of the EDL ultrafiltration membranes after cleaning is high. When the cleaning process according to the invention is used, the ultrafiltration modules or membranes have a long useful life, since the fall in performance from one cleaning operation to the next described at the beginning does not occur, or its progression is substantially flatter as compared with the cleaning processes of the prior art described at the beginning.

A further advantage of the process according to the invention is that conditioning (impregnation) of the EDL ultrafiltration membrane does not have to be carried out after the actual cleaning operation; on the contrary, the EDL ultrafiltration system can be coupled with the EDL bath contents again and can resume its intended operation immediately after the cleaning operation.

Example 1 (preparation of a cleaning agent for CDL ultrafiltration membranes, comparison):

A cleaning agent for CDL ultrafiltration membranes is prepared by mixing the following constituents:

86 parts by weight of deionised water,
4 parts by weight of pure acetic acid,
10 parts by weight of butyl glycol.

The resulting mixture is warmed to 50°C.

Example 2 (preparation of a cleaning agent for CDL ultrafiltration membranes, according to the invention):

A 35 wt.% CDL dispersion that has an amine content of 60 milliequivalents per 100 g of solids (solids formed by aminoepoxy resin binder and blocked polyisocyanate crosslinking agent), that contains 1 wt.% phenoxypropanol as solvent and that has been neutralised with acetic acid corresponding to a content of 30 milliequivalents of acid per 100 g of solids is mixed with 25 wt.% acetic acid and deionised water and thereby adjusted to a solids content of 25 wt.% and a degree of neutralisation of 240 %, and is stirred for 3 hours at 50°C.

Example 3 (cleaning of a CDL ultrafiltration module without impregnation, comparison):

A CDL ultrafiltration module (spiral wound module) having an ultrafiltration membrane area of 16 square metres is cleaned following a drop in performance, occurring as a result of a continual CDL ultrafiltration operation, from an initial flux rate of 460 litres of ultrafiltrate per hour to 300 litres of ultrafiltrate per hour. To that end, the CDL bath material in the ultrafiltration module to be cleaned is first rinsed out with ultrafiltrate. The cleaning agent from Example 1 is then circulated through the ultrafiltration module for 14 hours at 50°C, an initial pressure at the ultrafiltration module of 3 bar and a throughput of 12 cubic metres per hour. The cleaning agent in the ultrafiltration module is subsequently rinsed out with deionised water. Rinsing with CDL ultrafiltrate is then carried out, and the ultrafiltration module is then coupled with

the CDC bath contents again and normal ultrafiltration operation is resumed. The initial flux rate is 460 litres of ultrafiltrate per hour.

Example 4 (cleaning of a CDL ultrafiltration module with impregnation, comparison):

Example 3 is repeated with the difference that, after rinsing the cleaning agent out of the ultrafiltration module with deionised water, impregnation of the ultrafiltration module is carried out by rinsing with a 0.5 % aqueous solution of Kochkleen™ P3 (Koch, Düsseldorf). After subsequently rinsing with CDL ultrafiltrate, the ultrafiltration module is coupled with the CDC bath contents again and normal ultrafiltration operation is resumed. The initial flux rate is 460 litres of ultrafiltrate per hour.

Example 5 (cleaning of a CDL ultrafiltration module, according to the invention):

Example 3 is repeated with the difference that the cleaning agent from Example 2 is used instead of the cleaning agent from Example 1. Rinsing out of the cleaning agent after the cleaning operation and separate impregnation are not carried out. On the contrary, the ultrafiltration module is coupled with the CDC bath contents again and normal ultrafiltration operation is resumed. The initial flux rate is 460 litres of ultrafiltrate per hour.

Figure 1 shows curves showing the fall in the ultrafiltration performance with time (flux rate in litres of ultrafiltrate per hour, plotted against the duration of the ultrafiltration operation in days) of the CDL ultrafiltration module cleaned according to Examples 3, 4 and 5 (according to the invention) during the continuous CDL ultrafiltration operation resumed following cleaning.

Example 3: curve with square symbols,
Example 4: curve with triangular symbols,
Example 5: curve with circular symbols.

The curves for the ultrafiltration module cleaned according to Examples 3 and 4 show progressions that differ only insignificantly from one another.

Starting from a comparable initial level, the progression of the fall in the ultrafiltration performance with time in the case of the CDL ultrafiltration module cleaned according to Example 5 is substantially flatter.

Patent claims:

1. Aqueous cleaning agent for ultrafiltration membranes in ultrafiltration units of electro-dipcoating plants, characterised in that it contains electro-dipcoating lacquer (EDL) binder overneutralised with neutralising agent.

2. Cleaning agent according to claim 1, characterised in that the EDL binder is self-crosslinking or is in the form of binder plus crosslinking agent.

3. Cleaning agent according to claim 1 or 2, characterised in that it contains EDL binder corresponding to a solids content of from 5 to 35 wt.%.

4. Cleaning agent according to any one of the preceding claims, characterised in that it contains neutralising agent corresponding to a degree of neutralisation of the EDL binder of from more than 100 to 1000 %.

5. Cleaning agent according to any one of the preceding claims, characterised in that it contains the same neutralising agents as the electro-dipcoating bath of the electro-dipcoating plant whose ultrafiltration system is to be cleaned using the cleaning agent.

6. Cleaning agent according to any one of the preceding claims, characterised in that it contains the same EDL binder as the electro-dipcoating bath of the electro-dipcoating plant whose ultrafiltration system is to be cleaned using the cleaning agent.

7. Cleaning agent according to any one of the preceding claims, characterised in that the EDL binder is an anodically depositable binder and the neutralising agent is a base.

8. Cleaning agent according to any one of claims 1 to 6, characterised in that the EDL binder is a cathodically depositable binder and the neutralising agent is an acid.

9. Process for cleaning ultrafiltration membranes in ultrafiltration units of electro-dipcoating plants by rinsing with an aqueous cleaning agent, characterised in that a cleaning agent according to any one of claims 1 to 8 is used.

10. Process according to claim 9, characterised in that, when cleaning has been carried out, the cleaning agent is added to the electro-dipcoating bath of the electro-dipcoating plant whose ultrafiltration system has been cleaned using the cleaning agent, the same neutralising agent and the same EDL binder being used in the cleaning agent and in the electro-dipcoating bath.

11. Process according to claim 9 or 10, characterised in that the cleaning agent is circulated through the ultrafiltration unit.

Abstract:

Aqueous cleaning agent and its use in a process for cleaning ultrafiltration membranes in ultrafiltration units of electro-dipcoating plants, which cleaning agent contains electro-dipcoating lacquer (EDL) binders overneutralised with neutralising agent.

Rev. 06/95 H 33710 Docket Number FA-1058 99P823

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Cleaning agent and method for cleaning ultrafiltration membranes in electrophoretic dip coating installations

the specification of which is attached hereto unless the following box is checked: EP00/07994

☒ was filed on 16.08.2000 as U.S. Application No. _____ or PCT International Application No. _____ and was amended on 22.11.2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
199 38 886.5	DE	17.08.1999	yes

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.

U.S. Provisional Application No.	U.S. Filing Date

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)

POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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2-10

FA-1058

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GENERAL POWER OF ATTORNEY

(Concerning Several International Patent Applications)

The undersigned, Vernon R. Rice, Vice President and Assistant General Counsel of E. I. DU PONT DE NEMOURS AND COMPANY, 1007 Market Street, Wilmington, Delaware 19898 USA ("DuPont"), hereby confirms that the power to sign for DuPont has been granted to various individuals (as set forth in the attached excerpt from DuPont's Patent Board Rules of Procedure (January 1988), Appendix Section III.A.4), including the Chairman, Vice-Chairman, and those individuals who are Assistant Secretaries of the Patent Board. Currently these Assistant Secretaries are:

Roger A. Bowman	Barbara J. Massie
Linda J. Davis	Miriam D. Meconnahey
John E. Griffiths	Deborah A. Meginniss

(58)

In addition, the authority to act on behalf of DuPont before the competent International Authorities in connection with any and all international patent applications filed by it with the United States as Receiving Office and to make or receive payments on its behalf is hereby granted to:

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Joung, J. Kenneth	41,881	Wang, Chen	38,650

The undersigned ratifies fully all actions already taken by the above-named individuals in accordance with the authority granted hereby.

E. I. DU PONT DE NEMOURS AND COMPANY

By: V R Rice

Vernon R. Rice

Vice President and Assistant General Counsel

9-9-01

Rev. 10/93

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of:

HORST LEHMANN, ET AL. CASE NO.: FA1058

APPLICATION NO.: UNKNOWN GROUP ART UNIT: UNKNOWN

FILED: CONCURRENTLY HEREWITH EXAMINER: UNKNOWN

FOR: CLEANING AGENT AND METHOD FOR CLEANING ULTRAFILTRATION MEMBRANES IN ELECTROPHORETIC DIP COATING INSTALLATIONS

ASSOCIATE POWER OF ATTORNEY

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

I hereby appoint HILMAR L. FRICKE (Registration No. 22,384) as associate attorney in the above-entitled application, to prosecute this application, to make alterations and amendments therein, to inspect the file, and to transact all business in the Patent and Trademark Office connected therewith.

Please address all future communications to the above-appointed associate attorney of record at the following new address:

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Respectfully submitted,

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Dated: 12 February 2002